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Yet More Observations on the High-Low Quartz Inversion: Thermal Analysis Studies to 7 kbar with Single Crystals

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Abstract

The peculiar nature of the thermal analysis signal for the high-low inversion in quartz single crystals is verified. For each sample, no change in the nature of the signal or the temperature difference between heating and cooling signals is observed either by varying pressure (up to 7 kbar) or by changing heating/cooling rate. The initial slope, dT/dp, of the trajectory of the inversion is verified to be at least 26 deg kbar^{-1}; within the pressure range to 7 kbar, decisive evidence that the curvature, d^2T/dp^2, is nonzero is lacking. Precision and accuracy of measurement in these and similar data make detailed comparisons of results difficult.

Introduction

As the high-low quartz inversion is studied in greater detail, more complexities are encountered. This note reports precise studies on the inversion at high pressures using single crystals and thus is to be compared especially with the very recent work of Koster van Groos and ter Heege (1973) ("KvGtH") to 10 kbar with powdered samples. In the precise work being done with this inversion, the problems of uniformity among samples, thermocouple calibrations at ambient and elevated pressures, *etc,* are conspicuous, and it seems impossible to make detailed comparisons among the different sets of data.

Experiments

The internally-heated argon gas apparatus described by Goldsmith and Heard (1961) was used with minimal modifications. Pressures were read from 1, 3, or 7 kbar Heise bourdon tube gauges; after these experiments were completed, the 1 and 3 kbar gauges were calibrated to 1 bar within the 2.7 kbar limit of a deadweight tester. Temperatures in the gas apparatus were varied manually, using a ten-turn potentiometer to control a silicon-controlled rectifier. Instead of the thermocouple arrangement shown in Figure 1 of Goldsmith and Heard (1961), three thermocouple leads were introduced through a closure piston which was made from a tungsten carbide cylinder having a 3.2 mm diam. axial hole. A steel end-plug, slightly smaller than the diameter of the carbide piston, was soft-soldered or epoxied to the high pressure end of the piston. The steel plug contained an alumel and two chromel leads which were made to hold gas pressure in the manner of the original design. Steel 0–80 screws in the tapered plugs clamped the respective thermocouple wires to the leads.

Experimental samples were cylinders of clear, single-crystal Brazilian quartz cored parallel to the *c* axis. A slot approximately 0.2 mm wide was cut with a wire saw parallel to the axis of each cylinder and approximately to a depth of the radius; location of the slot was difficult to control and was not always

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on a radius. Sample temperature was measured with a butt-welded 0.127 mm diam. chromel-alumel thermocouple placed in the slot; the junction was located approximately mid-way from the ends of the sample. The cylinder used in run 1 was 2.4 mm diam. and 2.5 mm long; that in run 2 was 1.7 mm diam. and 1.7 mm long; the sample used in runs 3 and 4 was 1.2 mm diam. and 1.2 mm long, with a mass of ~3 mg. The reference junction, a butt-welded 0.32 mm diam. thermocouple, was located within a piece of 4-bore mullite thermocouple tubing of 1.6 mm o.d. and 0.39 mm bore. Mullite thus became the DTA reference material. The measuring junction was pulled tightly against the quartz, and its leads run into the other holes of the mullite tubing. In runs 3 and 4, silver conductive paint was applied to the measuring junction to assure good thermal contact between quartz and thermocouple. The reference junction and quartz cylinder were placed side-by-side and then the cylinder was wired to the mullite tube containing the reference junction. Reference and measuring junctions were therefore less than 2 mm apart. So as to minimize temperature fluctuations caused by convection in the horizontal furnace, the sample assembly was inserted into a 22 mm long, 5 mm i.d. gold tube which, in turn, was surrounded by a stainless steel tube closed at one end and push-fitted at the other. Isothermality was demonstrated by the DTA baseline varying less than $\pm 1/2°$ over the temperature range and also by all the quartz samples remaining intact during the runs; no cracking, often reported for samples in thermal gradients while passing through the inversion, was noted.

Emfs corresponding to temperature were recorded on a 25 cm wide two-pen strip chart recorder at 5 mV full scale for the first two runs, and 1 mV full scale for the second two runs. Emfs corresponding to differential temperature were recorded on full scales corresponding to as little as 0.1 mV. Heath/Schlumberger voltage reference sources provided calibrated voltage suppression for the temperature measuring circuit, and also compensated lead wires and an ice bath reference junction were used throughout. Thermocouple emfs were often read to ~0.001 mV. In order to avoid roundoff and interpolation errors arising from the use of standard thermocouple tables, which are tabulated at 0.10 mV intervals, a set of chromel-alumel thermocouple tables was computer-generated using the interpolation scheme and key values suggested by ASTM (1963). A similar routine was used to convert millivoltage directly to temperature. No attempt was made to correct for the effect of pressure on thermocouple emf because the data of Getting and Kennedy (1970) suggest that any correction within the present range would be less than 1°; this relatively small effect was an important consideration in the choice of chromel-alumel thermocouples here.

Heating and cooling rates were usually in the range of ~4 to 15 deg min^{-1} although some data were taken at other rates. In the heating/cooling cycles through the inversion, the maximum temperatures attained were 10° or less above the inversion temperature.

In run 1, data[2] were taken over the intervals, ~205 → 6955 bars and 6955 → 210 bars. In run 2, data were taken over the successive intervals, 1 → 6235 → 1 bars. A 7 kbar pressure gauge was used for both these runs. In run 3 (using a 3 kbar pressure gauge), data were taken over the successive intervals, 84 → 2711, 229 → 854 and near 2100 bars. In run 4 (using both 1 and 3 kbar gauges simultaneously), data were taken over the range 19-1/2 → 997 and near 508 and then 1 bar. When pressure was decreased rapidly, at least 15 min. were allowed for the Bourdon tubes in the pressure gauges to equilibrate to room temperature. This wait appears to be necessary for precise work, since upon decreasing pressure to ambient pressure, it had been noted that the pressure gauges initially read below zero, presumably because of adiabatic cooling.

In run 2, the 1 bar data after the first pressure cycle were $\lesssim 0.2°$ lower than the initial values. In run 3, the data in the second pressure cycle were $\lesssim 0.1°$ lower below 0.85 kbar and also near 2.1 kbar, where comparison with the data from the first cycle could be made. In run 3, the thermocouple drift was $< 0.1°$ near 0.5 kbar. Extensive experiments (Potts and McElroy, 1961; McElroy, 1958) on the drift with time of chromel-alumel thermocouples at 1 bar have shown the behavior to be complex and plausibly of the same order as encountered here.

Nature and Variations of the Thermal Analysis Signals

A typical temperature *vs* time signal is shown in Figure 1. The details of the signal beyond the initial

[2] To obtain a complete table of runs (37 pages), order NAPS Document 02418 from ASIS, c/o Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N. Y. 10017. Please remit in advance $1.50 for microfiche or $5.00 for photocopies. Please check the most recent issue of this journal for the current address and prices.